AFRL-SR-BL-TR-99-

REPORT DOCUMENTATION PAGE

$\theta /30$

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REP
	May 7, 1999	Final Technical Report 3/1/96 - 2/28/99

4. TITLE AND SUBTITLE

Synthesis, Thermodynamics and Processing of
Block Copolymer Based Nanocomposites

5. FUNDING NUMBERS

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**10. SPONSORING / MONITORING
AGENCY REPORT NUMBER**

AF/F49620-96-1-0088

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for Public Release; Distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 Words)

Two sets of model diblock copolymers were synthesized using anionic polymerization and heterogeneous catalytic hydrogenation: Poly(ethylene)-poly(ethylenepropylene) (PE-PEP) and poly(ethyleneoxide)-poly(alkane) (PEO-PA) where PA is PEP or poly(ethylethylene) (PEE). Blends of PE-PEP with the respective PE and PEP homopolymers were shown to form a bicontinuous microemulsion using small-angle neutron scattering (SANS) and transmission electronmicroscopy (TEM) measurements. Thermoset resins composed of bisphenol-A-*co*-epichorohydrin (BA348) and methylene dianiline (MDA) hardener have been modified through the addition of PEO-PEP diblock copolymers. Self-assembly of the diblocks leads to ordered lamellar (L), cylindrical (C), bicontinuous gyroid (G), and spherical (S) microdomains as evidenced by SAXS and SANS. Thermally induced curing results in clear, uniform nanocomposites with prescribed morphologies as revealed by TEM. Crosslinking was found to induce local segregation of PEO from the epoxy without any evidence of macrophase separation. In the limit of low block copolymer concentrations a monodisperse microemulsion is obtained with domain dimensions that scale with molecular weight. Compact tensile fracture tests revealed a 30% improvement in K_{1C} with the addition of just 5% block copolymer. These findings constitute unprecedented control over the morphology of thermoset plastic materials.

14. SUBJECT TERMS

Epoxy, block copolymers, nanocomposite

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

Final Technical Report

I.　Introduction

Thermosetting materials such as expoxies offer a host of desirable physical properties. They can be processed as inviscid liquids into complex shapes, then cured into hard, chemically inert parts with a high glass transition temperature. This class of plastics finds applications as adhesives, coatings, encapsulants, insulators, and structural elements in a wide range of products including aircraft, sporting goods, automobiles, and electronic devices . One of the principal design restrictions associated with manufacturing equipment with epoxy components is the intrinsic brittle nature of the unmodified materials. In order to improve the ultimate properties thermosets have been modified with rubber particles, plasticizers, and chemically reactive diluents that are incorporated into the three-dimensional network during thermal curing. None of these approaches are completely satisfactory. As a two-part epoxy cures the weight average molecular weight diverges (at the gel point) causing polymer that is miscible with the monomeric resin to phase separate. Therefore, rubber modifiers are usually added as preformed particles, making it difficult or impossible to produce nanoscale composites or non-spherical microdomain shapes.

Research conducted under this AFOSR grant has led to the discovery of a new method for templating nanostructure in thermosetting plastics. Amphiphilic block copolymers containing an epoxy resin miscible PEO block have been shown to produce well-defined lamellar, cylindrical, bicontinuous and spherical domains when blended with commercial epoxy and diamine hardener. These morphologies are perfectly preserved when thermally cured, leading to monolithic pieces of clear, nanostructured epoxy material.

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The resulting structures were characterized using TEM, SAXS and SANS and the associated mechanical properties assessed by dynamic mechanical spectroscopy, and tensile and impact testing.

II. Research Results

Research under the current contract addressed a variety of approaches to controlling nanoscale structure in multicomponent composites based on the strategic use of block copolymers. Phase behavior in such systems is generally depicted using a four parameter phase prism as illustrated in Figure 1. Three classes of mixtures have been investigated in the current program: i) pure block copolymers (A-B); ii) block copolymer mixed with an additive miscible with one block (A-B/C); and iii) block copolymer added to a pair of homologous homopolymers (A-B/A/B). The goal of this work is to establish the feasibility of controlling nanostructure in engineering plastics in order to enhance physical properties, particularly in thermosetting compounds such as epoxies. A comprehensive approach that relies on polymer synthesis and molecular characterization, small-angle X-ray and neutron scattering (SAXS and SANS), transmission electron and a variety of mechanical testing methods including dynamic mechanical spectroscopy (DMS), impact, and tensile and fracture testing has been implemented. The remainder of this report summarizes progress in all three areas of research, with an emphasis on the discovery of a new method, and illumination of underlying principles, for preparing nanostructured thermosets by templating with amphiphilic block copolymers.
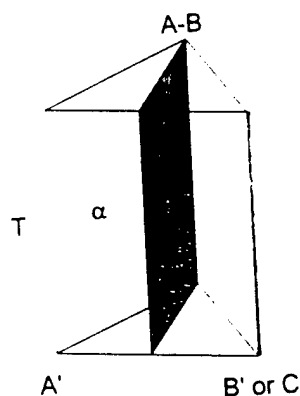

Figure 1. Phase prism used to describe the thermodynamics of diblock copolymer (A-B) and homopolymer (A', B' and C) mixtures. Polymeric bicontinuous microemulsions were discovered within the symmetric isopleth plane β while epoxy nanocomposites have been prepared in plane α.

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IIa. Synthesis and thermodynamics of block copolymer melts

A critical ingredient of any successful polymer research program is a reliable source of materials. Our first task in the current program was to develop efficient synthetic procedures for preparing sizable ($\sim$ 100 g) quantities of amphiphilic block copolymers composed of poly(ethyleneoxide) (PEO) and poly(alkane) (PA); here PA refers to poly(ethylene) (PE), poly(ethylethylene) (PEE) or poly(ethylenepropylene) (PEP) produced by hydrogenating the appropriate poly(diene) precursor. A five-step sequence of reactions that includes anionic polymerization and heterogeneous catalytic hydrogenation with near perfect (100%) yields was established as described in reference 1. These PEO-PA compounds represent the key ingredient in producing the nanostructured epoxies described in section II.c.

An important factor in using any block copolymer is the molecular weight required to produce microphase separation. Due to the strong thermodynamic incompatibility between PEO and PA, diblocks of these components order when the number-average molecular weight, M_n, is raised above about 2,000 g/mol as shown in references 2 and 3. These low molecular weight block copolymers provide an unprecedented opportunity to circumvent the kinetic constraints encountered when studying traditional block copolymer melts in the vicinity of order-order phase transitions.[3-6] Using a combination of DMS and SAXS we have demonstrated[3] that the hexagonally perforated lamellar (HPL) phase is a metastable state that occurs due to kinetic constraints associated with the lamellar-to-gyroid (L-to-G) phase transition. This result finalizes the Universal Phase diagram for diblock copolymers,[7] which we have now shown extends down to molecular weights as low as $M_n \cong 1,500$ g/mol.

IIb. Polymeric bicontinuous microemulsions

Perhaps the most dramatic control over composite properties is obtained in the vicinity of a phase inversion where a discontinuous minority component develops three-

dimensional connectivity. Recent work with pure block copolymers[8,9] has demonstrated that within narrow windows on either side of the phase diagram (plotted as composition f versus χN where χ and N are the segment-segment interaction parameter and degree of polymerization, respectively), a bicontinuous gyroid (G) morphology exists, located between the lamellar (L) and cylindrical (C) states. This intriguing structure complements the exciting opportunities to tailor the mechanical and optical properties of polymer composites using block copolymers.[10,11] However, the range of compositions within the phase prism (Figure 1) where the G phase occurs is relatively limited, and associated with rather high concentrations of block copolymer.[12]

Our first approach to developing facile methods for producing a bicontinuous nanocomposite involved blending two strongly segregated diblock copolymers near compositions associated with G phase formation in the intermediate segregation limit.[13] Theory[7] and experiment[9] indicate that the G phase window closes as the strong segregation limit (SSL) is approached. Experiments with M_n = 84,000 g/mol PE-PEE diblock copolymers support this conclusion. Slow solvent casting of binary blends containing f_{PE} = 0.35 and 0.51 (f_{PE} is the volume fraction of PE) produced either cylindrical (C), lamellar (L), or phase separated (C+L) morphologies. However, when the same blend is precipitated, molded, and annealed for as much as 1 month at 150°C, a uniform disordered bicontinuous state is obtained. This material, which is semicrystalline at room temperature, exhibits mechanical properties (elasticity, yield and failure strength) unlike those associated with either the C or L morphologies. A paper describing this new metastable bicontinuous state has been accepted for publication.[14]

We have followed an alternative approach in pursuing bicontinuous morphologies in blends of two incompatible plastics. Based on the well-documented phase prism that characterizes surfactants mixed with oil and water,[15,16] we speculated that a disordered bicontinuous microemulsion state might exist between the lamellar and two-phase regions along the isopleth plane that cuts symmetrically through the phase prism in A-B/A/B ternary

mixtures (see Figure 1). This thermodynamic state is not anticipated by mean-field theory[17] which predicts a multicritical Lifshitz point where the disordered, lamellar and two-phase regions meet. SANS, rheological, and TEM measurements on ternary blends of PE, PEP and a PE-PEP diblock copolymer confirmed this hypothesis.[18] Figure 2 depicts the phase diagram for symmetric blends of equal molecular weight PE and PEP ($M_n = 2.3 \times 10^4$ g/mol) when mixed with a symmetric ($f = 1/2$, $M_n = 1.1 \times 10^5$ g/mol) PE-PEP diblock copolymer; this model system splits the phase prism (Fig. 1) exactly in half. As PE and PEP homopolymer are added to the diblock copolymer the lamellar spacing increases, eventually transforming into a bicontinuous microemulsion state at about 90% by volume of homopolymer. The inset to Figure 2 is a TEM image obtained from a sample located within the microemulsion channel.

Although this discovery clearly demonstrates a new approach to obtaining bicontinuity in polymer blends, practical application of this result is limited by the narrow composition range available. However, in a collaboration with Glenn Fredrickson, the PI
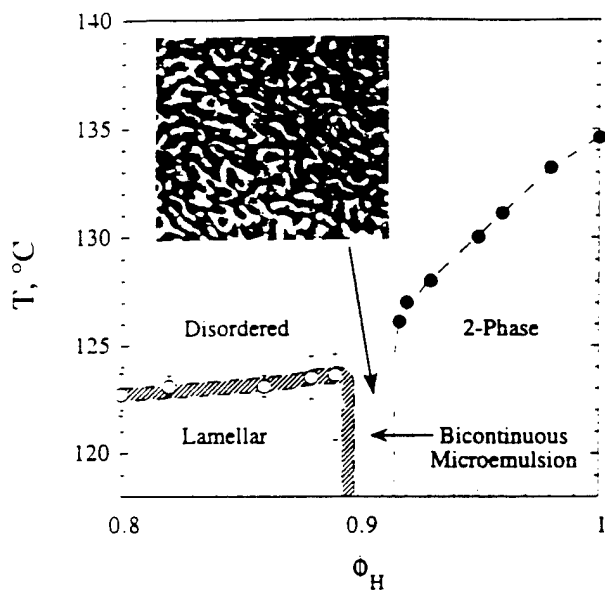

Figure 2. Phase behavior of PE-PEP/PE/PEP ternary mixtures along the symmetric isopleth (β plane in Figure 1). ϕ_H corresponds to the volume fraction of homopolymer. The inset is a TEM micrograph showing the bicontinuous microemulsion morphology (from ref. 18).
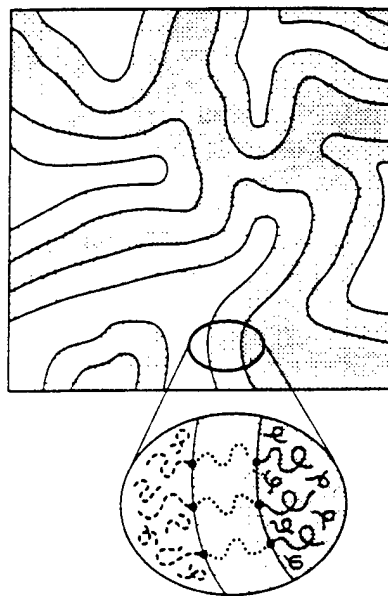
Figure 3. Tricontinuous microemulsion predicted for ternary mixture of ABC triblock copolymer and A' and C' homopolymer (from ref. 19).

has shown[19] that co-continuous morphologies can be stabilized over a broad portion of the phase prism through the use of ABC triblock copolymers. Judicious selection of block lengths (e.g., $N_A = N_C = 2/5 \, N_B$) and symmetric interaction parameters, $\chi_{AB} \approx \chi_{BC} \approx 0.25 \, \chi_{AC}$ should produce a tricontinuous state in triblock/homopolymer mixtures. Addition of low molecular weight A' and C' homopolymer ($N_{A'} < N_A$ and $N_{C'} < N_C$ where $N_{A'} = N_{C'}$) is expected to dilate this structure until it disorders into a tricontinuous microemulsion (see Figure 3). Thus, incorporation of an incompatible center block provides an opportunity to replace the lamellar region of the isopleth shown in Figure 2, with a tricontinuous window, thereby expanding the range of bi- or tri-continuity over much of the phase prism.

IIc.   Nanostructured thermosets

The principal objective of the current research is to establish the feasibility of manipulating the structure of thermosetting plastics by incorporating amphiphilic block copolymers. Modification of thermosets, such as epoxy, for the purpose of improving mechanical properties, e.g., toughness, is not a novel concept.[20-27] However, prior to this work essentially all attempts to incorporate fine dispersions of linear polymer in thermosets have been hampered by phase separation during curing. A major accomplishment of the present research program is the discovery that certain microphase separated block copolymers remain dispersed or ordered on a nanoscale throughout the crosslinking process as a two-part epoxy cures. This finding, along with the associated fundamental concepts under development, provide the impetus for the new research proposed in section III.

We have focused our effort in this area on a commercially relevant thermosetting epoxy formulation composed of bisphenol-A-co-epichlorohydrin (BPA348) and methylenedianiline (MDA) mixed in a stoichiometric ratio (2 moles epoxy resin : 1 mole hardner). Upon curing this system forms a clear solid with a glass transition temperature in

excess of 200°C. A variety of PEO-PA diblocks have been used to modify this material; here we focus on PEO-PEE and PEO-PEP as described in references 28 and 29.

PEO and BPA348 form a nearly ideal solution since both components are characterized by essentially the same solubility parameter,[30] $\delta_{PEO} \cong \delta_{BPA348} = 10.3$ $(cal/cm^3)^{1/2}$. Thus, when BPA348 is mixed with PEO-PEP or PEO-PEE the PEO blocks swell. Provided the undiluted diblock microphase separates, this induces changes in the interfacial curvature which lead to transitions between the familiar ordered phases found in pure block copolymers. Figure 4a illustrates the phase diagram determined for the binary system PEO-PEP ($f_{PEO} = 1/2$, $M_n = 2,700$ g/mole) and BPA348. The pure diblock exhibits a lamellar morphology with an order-disorder transition temperature (T_{ODT}) at 134°C. As the weight fraction of BPA348 is increased with $T < T_{ODT}$ the mixture changes from L to G to C to S and then disorders. Ordered phase symmetries have been identified by SAXS while the ODT curve has been determined by DMS. Increasing the diblock molecular weight raises the ODT curve to higher temperatures as shown in Figure 4b. These trends are anticipated by mean-field theory.[12]
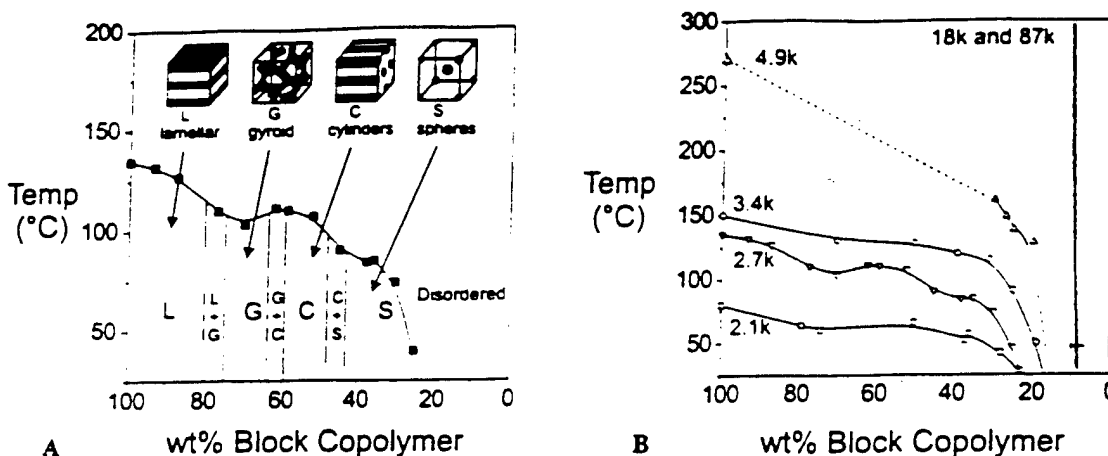

Figure 4. a) Phase behavior of binary mixtures of BPA348 and a symmetric PEP-PEO diblock copolymer. b) Order-disorder transition temperature for symmetric PEP-PEO and BPA348 as a function of diblock molecular weight.

The hardener, MDA, is also a good solvent for PEO but with a higher solubility parameter, $\delta_{MDA} \cong 11.3$ (cal/cm^3)$^{1/2}$. Therefore, although mixtures of PEO-PEP and MDA exhibit the same series of phases shown in Figure 4, T_{ODT} is considerably higher than with BPA348. For example, a PEO-PEP/MDA mixture containing 55% diblock has $T_{ODT} = 190°C$, which is about 80°C higher than for the corresponding PEO-PEP/BPA348 blend (see Figure 4). These results insure that the BPA348/MDA resin can be modified with block copolymer in a predictable manner. We have conducted similar experiments with various symmetric PEO-PA diblock copolymers.

A host of curing experiments have been carried out over the complete range of compositions from 0 to 100% block copolymer in the BPA348/MDA epoxy resin, using a variety of PEO-PEP and PEO-PEE materials. We have discovered that in all cases macroscopic phase separation does not occur as the condensation reaction causes the network molecular weight to diverge. Instead, crosslinking freezes the morphology in a well-ordered state that reflects the equilibrium nanostruct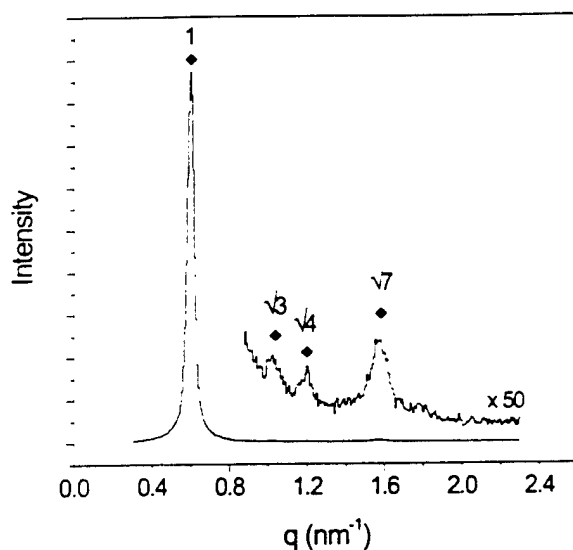ure established when the polymer and monomers were initially mixed. Because this system cures extremely slowly below about 100°C (gelation requires about 10 hours at 100°C but 95% conversion is obtained within 15 min at 180°C) mixtures can be handled with ease at room temperature, then examined by SAXS under controlled reaction rates. Figure 5 shows a SAXS pattern obtained from a cured nanocomposite containing 36 weight % PEO-PEP. The sequence of reflections and narrow line widths indicate a

Figure 5. Small-angle X-ray scattering (SAXS) pattern from a cured epoxy nanocomposite containing hexagonally packed cylinders.

well-ordered array of cylinders imbedded in the hard epoxy matrix. Transmission electron microscopy conducted on ultramicrotomed and RuO₄ stained slices of this material confirm this assessment as illustrated in Figure 6.

TEM images taken from specimen prepared with PEO-PEE have revealed an important feature of these nanocomposites: a core and shell morphology is evident where unstained PEE forms the cylindrical core surrounded by darkly stained PEO, all embedded in a gray epoxy matrix (see Figure 6). Apparently, the PEO is ejected from the epoxy network as the crosslink density increases, converting the swollen "wet" brush into a "dry" brush. This suggests that the block copolymer does actually "phase separate" as expected, only on a nanoscale. Previous experiments with additives blended with epoxy, even PEO homopolymer,[25] have resulted in macrophase separation as the curing reaction progresses. Why this undesirable effect is avoided in our mixtures is not entirely clear. We suspect that the combination of self-assembly and ordering on a small length scale results in a prohibitively high free-energy barrier for nucleation of separate phases rich in epoxy and block copolymer. Formation of macrophases also requires polymer transport
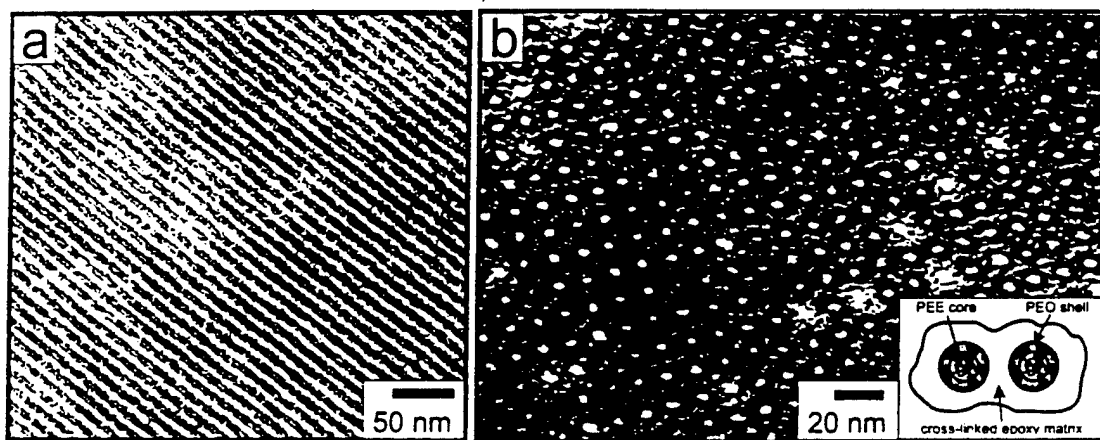

Figure 6. TEM images of cured epoxy nanocomposites containing hexagonally packed cylinders. a) View normal to cylinder axis. b) View along cylinder axis. Close inspection of these structures reveals a core and shell morphology as sketched in the inset (from refs. 28 and 29).

which is inhibited by network formation and the presence of microdomains. However, we do not believe the templating effects result from simple kinetic limitations since slow curing reactions lasting as long as a month lead to the same well-ordered nanocomposites.

In order to evaluate the effects of disorder on the templating process, we performed a series of reactions with various symmetric PEO-PEP diblocks ranging from $M_n = 2,700$ to 85,000 g/mol in the limit of low block concentrations. The 18,000 g/mol system exhibits an order-disorder transition between 6 and 8 wt % block copolymer at room temperature. SAXS experiments conducted on a 6% specimen before and after curing (Figure 7) reveal that network formation freezes the micellar solution without inducing phase separation. This illustration also demonstrates that the scattering patterns can be quantitatively modeled with Percus-Yevick liquid-state theory[31] demonstrating that the disordered spherical micelles are randomly distributed in the epoxy. Increasing the block
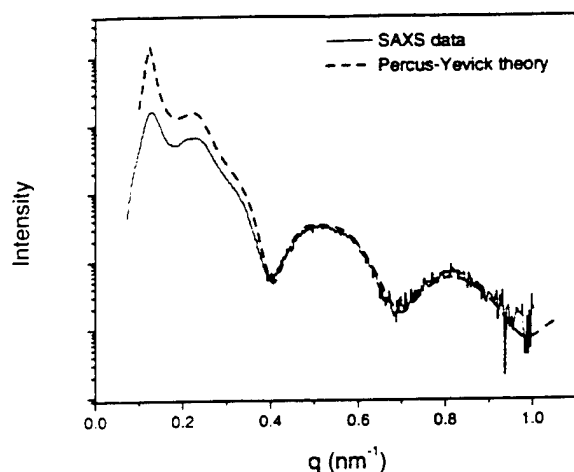
Figure 7. SAXS pattern from an epoxy nano-composite containing 6 wt % symmetric PEP-PEO diblock copolymer. Close agreement between the experimental and calculated curves confirms a random distribution of nearly monodisperse domains.
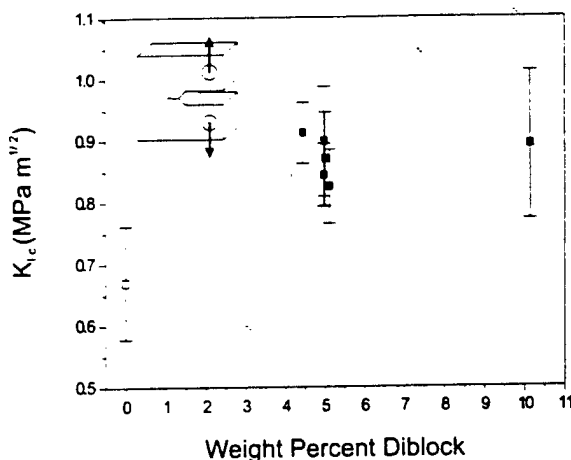
Figure 8. Compact tensile fracture test results for pure epoxy (□) and nanocomposites (▢) containing spherical PEP-PEO micelles. Each data point was determined from six fracture tests, except the 10% point which contains three experiments. Five molecular weights, from 2×10^3 to 8.7×10^4 g/mol are represented.

copolymer molecular weight from 2700 to 85,000 g/mol results in more than an order of magnitude increase in the PEP domain diameter.

These experiments reveal a novel mechanism for nanocomposite formation in block copolymer modified thermosetting polymers. Initially the monomers mix preferentially with the PEO blocks producing an equilibrium ordered (or disordered) microphase separated morphology. Upon heating condensation of amine and epoxy groups leads to network formation and eventually gelation (this occurs at 58% conversion for the mixtures discussed here). As the molecular weight of the resin increases the PEO blocks are ejected. This "wet brush" to "dry brush" transition closely resembles the predicted[12] and documented[32,33] effects on the miscibility of linear A homopolymer with A-B diblock copolymer as the homopolymer molecular weight is increased. As shown in reference 29 the associated change in interfacial curvature can actually induce order-order transitions (e.g., we have documented $G \rightarrow L$ and $S \rightarrow C$) during thermosetting. Thus, the block copolymer functions largely as a templating agent that establishes a domain type and packing symmetry, then extracts itself from the reacting medium leaving nearly pristine epoxy (see inset of Figure 6b).

The primary goal of this research is to improve the physical properties of epoxy, particularly the impact toughness. Preliminary experiments suggest that a relatively dilute dispersion of PEP spheres has a favorable effect on the failure properties of the material. We have prepared a series of specimens in 2 mm thick sheets with approximately 5 wt % of various symmetric PEO-PEP diblocks. These have been machined into compact fracture test specimens and subjected to an ASTM $K_{1,c}$ test[34] (see Figure 8). In all cases we find a statistically significant improvement in toughness essentially independent of block copolymer molecular weight, i.e., independent of the spherical domain size. Averaged over all specimens the diblock copolymer imparts a 30% improvement in fracture strength.

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IId. Publications resulting from this grant:

1.   M.A. Hillmyer and F.S. Bates, "Synthesis and Characterization of Model Polyalkane-Poly(ethyleneoxide) Block Copolymers," *Macromolecules* **29**, 6994 (1996).

2.   M.A. Hillmyer and F.S. Bates, "Influence of Crystallinity on the Morphology of Poly(ethyleneoxide) Containing Diblock Copolymers," *Macromol. Symp.* **117**, 121 (1997).

3.   M.A. Hillmyer, P.M. Lipic, D.A. Hajduk, K. Almdal, F.S. Bates, "Self-Assembly and Polymerization of Epoxy Resin-Amphiphilic Block Copolymer Nanocomposites," *J. Amer. Chem. Soc.* **119**, 2749 (1997).

4.   F.S. Bates, W.W. Maurer, P.M. Lipic, M.A. Hillmyer, K. Almdal, K. Mortensen, G.H. Fredrickson, T.P. Lodge, "Polymeric Bicontinuous Microemulsions," *Phys. Rev. Lett.* **79**, 849 (1997).

5.   G.H. Fredrickson and F.S. Bates, "Stabilizing Co-Continuous Polymer Blend Morphologies with ABC Block Copolymers," *Eur. Phys. J.B*, **1**, 1 (1998).

6.   D.A. Hajduk, R.-M. Ho, M.A. Hillmyer, F.S. Bates, K. Almdal, "Transition Mechanisms for Complex Ordered Phases in Block Copolymer Melts." *J. Phys. Chem. B*, **102**, 1356 (1998).

7.   P. A. Lipic, F.S. Bates, M.A. Hillmyer. "Nanostructured Thermosets from Self-Assembled Amphiphilic Block Copolymer/Epoxy Resin Mixtures," *J. Amer. Chem. Soc.*, **120**, 8963 (1998).

8.   P.A. Lipic, F.S. Bates, M. Matsen, "Nonequilibrium Phase Behavior in High Molecular Weight Diblock Copolymers and Binary Diblock Blends," *J. Polym. Sci., Polym. Phys.*, to appear.

9.   M.A. Hillmyer, W.W. Maurer, T.P. Lodge, F.S. Bates, K. Almdal, "Model Bicontinuous Microemulsions in Ternary Homopolymer/Block Copolymer Blends," *J. Phys. Chem. B*, to appear.

IIe. Personnel

IIf.1 Students Supported

Paul Lipic	Ph.D., fall 1998; now at Proctor and Gamble.
Jennifer Dean	Began graduate school in Chemical Engineering fall 1997.

IIf.2 Postdocs Supported

Marc Hillmyer	Now an Assistant Professor of Chemistry, University of Minnesota.
Damian Hajduk	Now at Symyx Corp., Sunnyvale, CA.
Martin Vigild	Began March 1998.
Barney Grubbs	Began September 1998.

IIf.3 Major Awards to Frank S. Bates (PI)

1997   High Polymer Physics Prize, American Physical Society

1996   Distinguished McKnight University Professorship, University of Minnesota

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2. M.A. Hillmyer, F.S. Bates, *Macromol. Symp.* **117**, 121, 1997.

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